PB80-194624

Compound Forms of Fossil Fuel Fly Ash Emissions

Battelle Columbus Labs., OH

Prepared for

Environmental Sciences Research Lab.
Research Triangle Park, NC

Apr 80

U.S. Department of Commerce
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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPI
EPA-600/J-80-005	JOURNAL ARTICLE	PB80-194624

4. TITLE AND SUBTITLE	5. REPORT DATE
COMPOUND FORMS of FOSSIL FUEL FLY ASH EMISSIONS	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
William M. Henry and Kenneth T. Knapp	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Battelle, Columbus Laboratories 505 King Avenue Columbus, Ohio 43201	C07A1D/09-0406 (FY-80) 11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, N.C. 27711	14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES

REFERENCE: Environ. Sci. Tech., 14(4):450-456, April 1980.

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
* Air pollution		13B
* Inorganic compounds		07B
* Fossil fuels		21D
* Fly ash		08G
* Chemical analysis		21B
Infrared spectroscopy		07D
		14B

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NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22151

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

Reprinted from ENVIRONMENTAL SCIENCE & TECHNOLOGY, Vol. 14, Page 450, April 1980

14(4):450-456

Compound Forms of Fossil Fuel Fly Ash Emissions

EPA-600/J-80-005
JOURNAL ARTICLE

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■ A methodology program for the determination of inorganic compounds present in particulate emissions from fossil fuel combustion processes is described. Samples collected from power plants burning oil and coal fuels of different compositions provided a typical range of fly ashes for the investigations. Elemental (cation/anion) determinations of these were used to guide the compound methodology work. Water extractions of the samples proved to be effective in the separation of soluble sulfate compounds from insoluble oxides and silicates, and this reduced the complexity of the compound forms remaining in the water-soluble and water-insoluble phases. A library of Fourier transform infrared reference spectra, prepared and stored for ready recall, was found to be essential for identification of compound species.

Based on elemental compositional data, potentially hazardous substances are postulated to be in the fly ashes derived from fossil fuel combustion processes. Despite concerns about the environmental significance of the millions of tons of particulate matter emitted annually, little is known as to the specific chemical forms of these particulate emissions. For lack of better data, the current practice for assessing the health effects of fly ash is based largely on the quantities of the emission elements and not on their chemical forms. Certain chemical forms of metals are known to be more toxic than others; soluble forms are generally regarded as having potentially more adverse effects than those tied up as insoluble oxides or in glassy structures. Knowledge of the chemical forms of fly ash emissions also can contribute to the planning of control strategy and to interpreting and predicting chemical interactions in the atmosphere, downwind fallout rates and potential damage to vegetation, and deterioration of materials and structures.

An extensive literature review (*1*) revealed that very little information is available on the chemical forms of inorganic compounds in fly ash emitted from oil-fired power plants. The principal purpose of the work described here is to identify the major constituents of these emissions and to compare the results with more readily available data on coal-fired emissions.

Since the fossil fuel combustion particulate products are principally inorganic substances, they are usually identified as oxides. Such designations, when obtained simply by the conversion of determined elements to their stable oxide forms, can lead to an impression that the fly ashes are simple insoluble unreactive pollutant products. This is far from reality in respect to oil-fired power plant particulate emissions and only partially representative of coal-fired emissions. Actually, products of fossil fuel combustion processes are chemically complex. In addition to carbon oxides, water, oxygen, and nitrogen—the principal products emitted from burning hydrocarbon fuels—many other contaminants are present in the combustion zone. These contaminants include oxides of sulfur and nitrogen, the many inorganic contaminants present in the fuel, plus any additives used to condition the ash or to promote combustion. These substances and operating parameters such as the air-to-fuel ratio, the combustion zone temperature, the time of residence in the burning zone, and the control mechanism and its efficiency all affect the quantity, size distribution, and chemical forms of the particulate emissions. The reaction process is quite short, but, presumably, by the time the stack sampling port is reached, most of the condensible inorganic components have interacted completely with the nonparticulate acidic gases present to form unreactive oxides, silicate/glasses, sulfates, water, and free acids.

Experimental

Sampling. Samples were collected from oil-fired and coal-fired power plants at the 3.5- to 4-in. diameter sampling ports normally provided for source emission testing, beyond any control system. An EPA Method 5 glass-lined sampling train probe inserted into the center of the stack was used to draw the stack emission particulates into a large fine-mesh Teflon bag held in a stainless steel, cylindrical container. Both the probe and the container were held at stack temperature during a 24-h collection period, but no special effort was made to sample isokinetically. The 25- to 50-g samples so collected, along with more aged fly ash samples plus the NBS SRM 1633 coal fly ash, were used in the identification work.

Water Solubilities and Sulfate Contents. Because of the chemical complexities of fly ash emissions, it was found important to carry out species separations in order to simplify the structural identification work. Separation on the basis of water solubility proved quite enlightening for this purpose. As shown in Table I, exclusive of the sootlike insoluble carbon present, the fly ashes collected from oil-fired power plant stacks were found to be from 66 to 100% water soluble, with SO_4^{2-} the only anion of more than trace concentration found present in the water-soluble phase, indicating that the water-soluble components are largely sulfates. X-ray diffraction and chemical analyses showed the insoluble phase of the oil-fired fly ashes to be metal oxides and uncombined carbon.

The coal-fired fly ashes were found to contain less water-soluble material, with one exception. This is an FGD system and, again, sulfate was the only major anion present in the water-soluble phase. The insoluble phase consisted primarily of amorphous and glassy structures plus some metal oxides.

Oil-Fired and Coal-Fired Fly Ashes Are Different. Residual fuel oils used in electrical generation combustion sources have low ash contents as compared to coal fuels and as such do not present the large-tonnage disposal problems of coal combustion byproducts. However, most oil-fired power plants operate without particulate control systems; thus, the quantities of fly ash emitted from their stacks can be significant.

As illustrated by typical micrographs shown in Figures 1 and 2, fly ashes emitted from oil-fired power plants differ physically from those emitted from coal-fired power plants, being generally of a more open and porous structure. Coal-fired fly ashes are closed, glassylike structures. Note the crystallites in the oil-fired fly ash shown in Figure 1. X-ray elemental analysis showed these crystallites to be principally magnesium, sulfur, and vanadium, which is in accord with the finding of large amounts of magnesium and vanadium sulfates in this oil fly ash.

Trace metals present in fuel oils are considerably enriched in their ash products. For instance, a fuel oil having a thermal

Table I. Water Solubility and Carbon and Sulfate Contents of Fly Ash Samples

no.	content	C, %	SO_4^{2-} %	water solubility, %
	Oil-Fired Fly Ashes			
1	total sample	12.4	36.9	58.0 (66.2)[a]
	water-soluble	0	36.0	
	water-insoluble	12.4	0.9	
2	total sample	69.0	12.0	23.3 (75.0[a]
	water-soluble	0	12.0	
	water-insoluble	69.0	0	
4	total sample	21.5	41.2	72.0 (91.7)[a]
	water-soluble	0	41.1	
	water-insoluble	21.5	0.1	
5	total sample	1.5	57.6	98.5 (100)[a]
	water-soluble	0	58.0	
	water-insoluble	1.5	0	
6	total sample	14.5	49.2	83.0 (97.1)[a]
	water-soluble	0	48.4	
	water-insoluble	14.5	0.8	
	Coal-Fired Fly Ashes			
SRM 1633	total sample[b]	3.3	0.98	3.5
	water-soluble	—	0.60	
	water-insoluble	—	0.38	
1	total sample	1.7	3.05	5.3
	water-soluble	0	2.13	
	water-insoluble	1.7	0.92	
2	total sample	7.0	6.9	13.0
	water-soluble	0	5.8	
	water-insoluble	7.0	1.1	
3	total sample	0.5	22.1	34.0
	water-soluble	0	19.6	
	water-insoluble	0.5	2.5	
4	total sample	0.1	50.6	79.2
	water-soluble	0	50.2	
	water-insoluble	0.1	0.4	
5	total sample	0.1	5.23	9.1
	water-soluble	0	2.32	
	water-insoluble	0.1	2.9	

[a] Percentage contents exclusive of the carbon. [b] This is a blend of ashes obtained from electrostatic precipitators or by a mechanical collector.

Figure 1. Oil fly ash no. 4 (1600×)

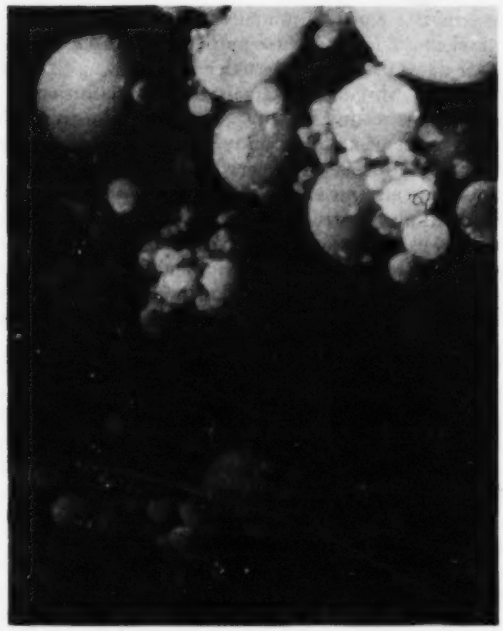

Figure 2. Coal fly ash no. 2 (1600×)

ash of 0.1% gives a fuel-to-ash concentrational factor of 1000× which, with a fuel oil content of 50 to 400 ppm of vanadium, could result in a fly ash content of 5–40% vanadium. Of course the fossil fuel combustion process does not result in as low an ash content as that obtained by thermal ashing at 725 °C, which drives off all the carbon, water, and some sulfates, but oil-fired fly ash contents of greater than 12% vanadium are found. Since, as seen later, a large proportion of the vanadium is present as $VOSO_4$, the vanadium products can represent a major portion of fly ash from fuel oil combustion. The higher ambient concentrations of vanadium found in the East and Southeast have been attributed to fuel oil consumption in those areas and are in contrast with the much lower concentrations found in the Midwest where coal is the predominant fossil fuel used (*2*).

The other principal metals contained in fuel oils include Ni and Fe, present in 10- to 100-ppm amounts, and Ca, Al, Na, K, and Mg which are present in 1- to 10-ppm amounts. (Mg, when added to fuel oils as an ash conditioner, is of course in higher concentrations.) All of these metals are enriched about 1000× in the fly ash combustion products.

Coal fuels used for power production average about 10–15% ash content, resulting in much lower concentration factors for contaminants in coals than for those in oil fuels. Usually present in coal are Fe, Al, and Si at about 1% concentrations and Ca, Mg, Ti, Na, and K in 0.02–0.5% concentrations. With a fuel-to-ash concentration factor of about 10×, the matrices of coal fly ashes are primarily iron–aluminum–silicates or calcium–iron–aluminum–silicates, which account for 60–90% of most coal-fired fly ashes.

Compound Identification Methodology. X-ray diffraction (XRD), Fourier transform infrared (FT-IR), and chemical-phase or valence-state analyses were the principal tech-

Table II. Oil- and Coal-Fired Fly Ash Compositions, Major Constituents (Percent)

no.	content	C	H	N	NO_3^-	NO_2^-	NH_4^+	SO_4^{2-}	SO_3^{2-}	S^{2-}	Cl^-	P	Si
						Oil-Fired Fly Ashes							
1	total sample	12.4	0.9	0.1	0.005	<0.01	0.012	36.9	<0.01	<0.01	0.05	0.008	0.31
	water-soluble							36.0	<0.01	<0.01			0.01
	water-insoluble							0.9	<0.01	<0.01			0.31
2	total sample	69.0	0.7	0.9	0.013	0.005	0.13	12.0	<0.01	<0.01	0.02	0.002	0.2
	water-soluble							12.0	<0.01	<0.01			0.01
	water-insoluble							0.15	<0.01	<0.01			0.2
4	total sample	21.5	1.0	0.9	0.02	0.01	0.81	41.2	<0.01	<0.01	0.02	0.004	0.2
	water-soluble							41.1	<0.01	<0.01			0.01
	water-insoluble							0.1	<0.01	<0.01			0.2
5	total sample	1.5	1.2	0.1	0.02	<0.01	0.16	57.6	<0.01	<0.01	0.05	0.001	0.05
	water-soluble							58.6	<0.01	<0.01			0.01
	water-insoluble							0	<0.01	<0.01			0.05
6	total sample	14.5	2.4	6.5	<0.01	0.03	7.3	49.2	<0.01	<0.01	0.06	0.05	0.22
	water-soluble							48.4	<0.01	<0.01			0.01
	water-insoluble							0.8	<0.01	<0.01			0.22
						Coal-Fired Fly Ashes							
NBS SRM 1633	total sample	3.3	0.1	<0.1[1]	<0.01	<0.01	<0.01	0.98	<0.01	<0.01	0.005	0.12	20.9
	water-soluble							0.60	<0.01	<0.01			
	water-insoluble												
1	total sample	1.7	0.3	<0.1	<0.01	<0.01	<0.01	3.05	<0.01	<0.01	<0.003	0.14	19.7
	water-soluble							2.13	<0.01	<0.01			
	water-insoluble												
2	total sample	7.0	0.5	0.1	<0.01	<0.01	0.06	6.9	<0.01	<0.01	0.007	0.02	16.7
	water-soluble							5.75	<0.01	<0.01			
	water-insoluble												
3	total sample	0.5	0.7	<0.1	0.02	<0.01	0.01	22.1	<0.01	<0.01	0.05	0.08	16.6
	water-soluble							19.6	<0.01	<0.01			
	water-insoluble												
4	total sample	0.1	1.2	<0.1	0.03	<0.01	0.15	50.6	<0.01	<0.01	0.06	0.2	6.2
	water-soluble							50.2	<0.01	<0.01			<0.01
	water-insoluble												6.2
5	total sample	0.1	<0.1	<0.1	<0.01	<0.01	0.01	5.23	<0.01	<0.01	<0.01	0.05	10.8
	water-soluble							2.32	<0.01	<0.01			
	water-insoluble												

no.	content	Al	Fe	Ni	V	Mg	Ca	Na	K	total org	water solubility	H_2O	H_2SO_4	pH
							Oil-Fired Fly Ashes							
1	total sample	1.25	0.61	1.66	2.27	18.4	1.0	3.91	0.13	<0.1	58.0	7.0	<0.1	3.9
	water-soluble	0.5	0.30	1.0	0.50	4.71	0.6	3.9	0.13					
	water-insoluble	0.75	0.31	0.66	1.77	13.7	0.4	0.01	0					
2	total sample	0.05	0.40	0.85	6.68	3.41	0.31	0.30	0.1		23.3	5.0	0.2	2.7
	water-soluble	0.02	0.25	0.60	2.23	1.15	0.15	0.30	0.1					
	water-insoluble	0.03	0.15	0.25	4.45	2.26	0.16	0	0					
4	total sample	0.40	0.41	1.29	10.2	5.94	0.1	0.50	0.10	0.053	72.0	4.5	0.04	2.42
	water-soluble	0.23	0.20	1.06	8.98	5.0	0.07	0.51	0.12					
	water-insoluble	0.17	0.21	0.23	1.22	0.94	0.03	0	0					
5	total sample	0.01	0.48	2.28	12.85	2.50	0.20	2.02	0.10	<0.1	98.5	5.5	1.0	2.15
	water-soluble	<0.01	0.49	2.31	12.9	2.65	0.19	2.0	0.09					
	water-insoluble	0.01	0	0	0	0	0.01	0	0					
6	total sample	1.42	0.40	0.35	1.10	2.4	0.32	0.20	0.12	<0.1	83.0	2.1	1.5	2.22
	water-soluble	0.27	0.43	0.30	0.78	2.4	0.16	0.21	0.11					
	water-insoluble	1.15	0	0.05	0.32	0	0.16	0	0					
							Coal-Fired Fly Ashes							
NBS SRM 1633	total sample	12.7	6.5	0.01	0.02	2.0	4.2	0.30	1.75	<0.1	3.5	0.03	<0.1	11.35
	water-soluble													
	water-insoluble													
1	total sample	11.3	12.6	0.06	0.02	0.52	1.5	0.60	1.54	0.04	5.3	1.0	<0.1	4.5
	water-soluble													
	water-insoluble													

Table II. Continued

no.	content	Al	Fe	Ni	V	Mg	Ca	Na	K	total org	water solubility	H_2O	H_2SO_4	pH
2	total sample	10.9	14.1	0.02	0.03	0.2	0.40	0.05	1.0	0.072	13.0	4.0	2.0	3.17
	water-soluble	0.63	0.56	0.01	0.01	0.01	0.18	0.03	0.5					
	water-insoluble	10.27	13.54	0.01	0.02	0.01	0.22	0.02	0.5					
3	total sample	8.79	7.90	0.05	0.05	0.5	3.0	0.08	1.1	0.11	34.0	5.0	2.1	2.73
	water-soluble	1.63	1.94	0.04	0.04	0.2	1.8	0.06	0.6					
	water-insoluble	7.16	5.96	0.02	0.02	0.4	1.2	0.02	0.5					
4	total sample	1.2	7.56	0.02	0.03	0.3	2.65	0.1	1.0	<0.1	79.2	3.9	16.5	2.2
	water-soluble	0.6	6.55	0.02	0.02	0.3	2.6	0.1	0.4					
	water-insoluble	0.6	1.0		0.01	0	0.05	0	0.6					
5	total sample	13.0	3.64	0.05	0.04	2.0	21.3	1.0	1.0	<0.1	9.1	1.0	0.1	11.3
	water-soluble	0.4	0.02	0.01	<0.01	0.01	1.0	<0.1	<0.1					
	water-insoluble	12.6	3.6	0.04	0.03	2.0	20.3	1.0	1.0					

niques used. Elemental (cation/anion) determinations were obtained to indicate the possible chemical species and quantities present. The determination results are given in Tables II and III.

For XRD analyses, 5-mg samples of the water-insoluble phases of the fly ash samples were deposited uniformly over a 20 mm diameter area of 25 mm diameter silver membrane filters, and these were analyzed using copper radiation at 35 kV and 40 mA power with sample spinning. Semiquantitative analyses were made for similarly prepared metal oxide mixtures. The method used closely followed that detailed by Williams (*3*).

The FT-IR technique was particularly useful in identifying fly ash in inorganic compounds due to its good sensitivity (30× over conventional IR systems), high resolution, accuracy, and the data handling capabilities of the Fourier transform system; details of the procedure are given by Jakobsen et al. (*4*) and Henry et al. (*5*). The dedicated computer of FT-IR systems allows for both storage of spectra and subtraction of spectra. This capability to store and subtract spectra is invaluable in characterizing the sample fractions, e.g., the water-insoluble fraction spectra can be run and subtracted from the total sample spectrum to give a computer-derived water-soluble spectrum for comparison with an experimentally obtained, water-soluble spectrum. Any changes in chemical form due to the dissolution and drying steps of the water solubility separation can be recognized and corrected for in this way. It is of note that, in the fly ashes examined, very minor changes in chemical form occurred in the dissolution and drying step. Also, individual stored reference spectra can be successively subtracted from a complex unknown compound mixture. The FT-IR technique also provides spectral identification of amorphous species such as the high concentration of largely glassy components of many coal-fired fly ashes.

Despite the apparent advantages of FT-IR for inorganic compound identification, its applicability is limited by the lack of appropriate reference spectra. This necessitates building a large spectral library of reference compounds of known assay, including known states of hydration. Attempts to resolve the problem of spectral differences due to different hydration states by heating the samples, sample fractions, and off-the-shelf reference compounds under an inert atmosphere at 200–300 °C were partially successful, but such treatment must be accompanied by thorough thermal analyses to be useful. On the plus side, a library of only several hundred spectra of inorganic sulfates, oxides, nitrates, carbonates, and other compounds of known hydration states plus a number of amorphous glass-type melts is required for useful identification of fossil fuel derived particulate pollutants.

Compound Identifications of Oil-Fired Fly Ash Samples. FT-IR spectra and XRD strip chart pattern recordings, obtained on the samples and their water-soluble and -insoluble fractions, were compared with those of reference compounds and with reference data indexes. The FT-IR identifications were made using spectral references obtained on chemically assayed and thermally analyzed reference compounds and, for the most part, these same reference compounds were used to obtain XRD pattern reference data, although the powder diffraction file data also were used.

As an example, FT-IR spectra and XRD patterns were obtained on thermally analyzed and chemically assayed V_2O_5, $VOSO_4 \cdot 3H_2O$, and $VSO_4 \cdot 2H_2O$ reference compounds. These patterns were used to search for and to identify these compounds in the total, water-soluble, and water-insoluble fractions of the five oil-fired fly ash samples. V_2O_5 was identified by XRD in the total and water-insoluble fractions of samples 1, 2, 4, and 6. $VOSO_4 \cdot 3H_2O$ was identified in the total and water-soluble fractions of all five fly ash samples, although the FT-IR spectra of sample 4 also indicated the presence of a vanadium salt similar but not identical with $VSO_4 \cdot 2H_2O$. This finding was not supported by the XRD analysis, and, tentatively, this discrepancy in structural identification is attributed to the effect of a partial hydration change in the FT-IR sample.

Organic species were found to be virtually nonexistent in the fly ashes, as indicated by the low percentages obtained by use of repeated organic solvent extractions. Essentially no carbonate was found in the samples. Microscopic and XRD analyses indicated most (50% and greater) of the carbon present to be in the form of uncombined, partially graphitic carbon.

Vanadium was chemically determined to be present, largely in the water-soluble phases of the several samples analyzed. A distinctive greenish to greenish blue color was noted in the water extracts. Valence state measurements, made by determination of V(V) in the presence of reduced vanadium and after oxidation to the V(V) state, showed the presence of amounts of reduced vanadium which compared well with the determined water-soluble vanadium values (Table IV).

The chemical analyses given in Tables II and III were used in the following manner as a validity check and an indication of the quantities of components present. The water solubility separations and chemical analyses thereof indicate that salt (metal and ammonium), sulfates, free sulfuric acid, and water constitute the principal components of the water-soluble sample fractions. Similarly, the analytical data plus microscopic observations indicate that metal oxides and carbon are the major components of the water-insoluble fractions. Based

Table III. Oil- and Coal-Fired Fly Ash Compositions, Trace Constituents

element	oil-fired fly ashes					coal-fired fly ashes					
	no. 1	no. 2	no. 4	no. 5	no. 6	NBS	no. 1	no. 2	no. 3	no. 4	no. 5
Li	0.5	0.5	0.2	3	100	300	0.1	200	200	150	20
Be	0.05	0.3	0.2	0.3	0.1	5	0.5	1.5	1.5	1	10
B	30	0.5	5	3	1	100	100	300	200	200	400
F	2	<1	3	5	<1	10	20	30	60	200	20
Sc	1	<1	5	3	<1	20	10	30	40	10	50
Ti	500	300	400	400	700	6000	2000	100	3000	3000	7000
Cr	100	500	1000	500	450	130	100	150	1000	400	200
Mn	200	200	200	500	300	500	50	300	200	100	500
Co	500	50	200	300	300	50	5	70	30	15	10
Cu	500	100	200	400	400	120	30	200	300	400	200
Zn	40	40	200	400	200	200	20	800	1200	7.3[a]	300
Ga	5	5	50	60	40	50	10	100	60	5	5
Ge		1	10	10	7	20	10	70	70	100	40
As	30	20	30	30	20	60	20	100	100	2000	30
Se	7	5	10	3	7	10	5	20	20	40	5
Br	10	3	25	25	2	10	15	5	20	25	10
Rb	5	1	5	4	7	150	5	400	700	60	200
Sr	500	100	300	300	200	1500	2000	200	150	200	3000
Y	50	3	5	10	10	30	50	100	30	5	100
Zr	50	5	20	20	10	200	100	200	50	60	200
Nb	10	2	1	1	2	7	5	10	7	5	5
Mo	100	50	100	100	150	20	10	40	70	500	70
Ru	<1	<1	<1	<1	<1	<0.5	<0.5	<0.5	<0.5	<1	<1
Rh	<1	<1	<1	<1	<1	<0.5	<1	<0.5	<0.5	<1	<1
Pd	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Ag	<1	<1	<1	<1	<1	<0.5	<1	0.7	0.7	20	1
Cd	1	1.5	4	3	4	15	2	8	10	2200	15
In	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<1	<1
Sn	20	3	5	5	3	3	3	10	10	100	15
Sb	3	5	10	10	150	7	1	10	15	500	10
Te	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	61	<1
I	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<1	<1
Cs	<1	<1	<2	3	1	10	1	20	40	20	60
Ba	1000	200	200	1000	1000	2500	1000	1000	500	200	3000
La	40	10	50	50	150	70	40	60	30	20	100
Ce	50	5	25	30	100	125	75	100	30	20	100
59–71	120	15	70	60	90	90	40	130	60	100	250
Hf	<0.5	<0.5	<0.5	<0.5	<0.5	10	3	2	2	1	10
Ta	<1	<1	<1	<1	<1	2	<1	1	1	1	3
W	<1	<1	2	2	2	5	<1	4	4	1	7
Re	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<1	<1
Os	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<1	<1
Ir	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<1	<1
Pt	0.3	0.3	<0.3	<0.3	<0.4	0.4	0.3	0.4	0.4	<1	<1
Au	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<1	<1
Hg	<1	<1	<1	<1	<1	0.1	<1	<1	<1	<1	<1
Tl	10	<0.2	0.5	1	0.2	2	2	15	30	30	40
Pb	3000	200	400	400	300	80	200	150	100	7400	70
Bi	<0.1	<0.1	<0.1	0.3	<0.1	0.7	<0.1	0.7	1	<1	2
Th	10	5	6	4	2	20	10	40	20	20	40
U	10	5	2	10	2	15	10	40	30	30	50

[a] Zn = 7.3% in total sample of which 6.9% is water soluble.

on the indications, the analytical data were used to calculate possible compound combinations present in the fly ashes. These data, shown in Table V, are in general accord (semi-quantitatively) with the spectral and pattern peak heights of the FT-IR and XRD found in the samples.

The chemical species specifically identified in five oil-fired fly ash emission particulate samples are listed in Table VI with the methods used to confirm their chemical forms either in the total samples and/or in separated water-soluble and water-insoluble phases.

Inorganic Compounds in Coal-Fired Fly Ashes. Coal-fired fly ash emissions, except for one sample, have considerably lower water solubilities than oil-fired fly ashes. As with the oil-fired fly ashes, the water-soluble phases of the coal-

Table IV. Valence States of Vanadium in Oil Fly Ash Samples, Percent

	V(V) [a] (total)	V(V) in the presence of reduced V [b]	reduced V (V(IV)) (by difference)	V (water soluble)
oil fly ash no. 1	2.27	1.70	0.57	0.50
oil fly ash no. 2	6.68	4.50	2.18	2.23
oil fly ash no. 4	10.2	0.90	9.30	8.98
oil fly ash no. 5	12.85	0.14	12.71	12.90
oil fly ash no. 6	1.10	0.35	0.75	0.78

[a] After oxidation of reduced vanadium to V(V) to give total vanadium, determination by atomic absorption. [b] Adaptation of an extraction–photometric procedure described in ref 6.

fired fly ashes consist mostly of sulfates, and these were identified by XRD and FT-IR analyses. The major component of coal-fired fly ashes (again with one exception) is a glassy amorphous phase, which by metal analysis is shown to be mostly iron, aluminum, calcium, and silicon structures. XRD analyses of this insoluble, largely amorphous phase, as expected, show minimal pattern structures. However, FT-IR analyses show good absorption spectra, which suggests that, with proper reference spectra, components of the amorphous phases may be identified. Hulett et al. have made very extensive chemical speciation studies of coal-fired fly ashes (7) in which they show that three different fly ash matrices, glass, mullite–quartz, and magnetic spinel, can be isolated. Hulett (personal communication) states that the glass phase, which is comingled with the mullite–quartz, can be removed by etching in 1% HF and suggests that the FT-IR technique be used to look at the aluminosilicate component of fly ash, with magnetic spinel extracted, before and after etching. The residue left after etching will be mullite and quartz in a relatively pure form and the glass-phase spectrum possibly may be determined by difference.

Scrubber-Controlled Power Plant Sample. The no. 4 coal-fired fly ash sample was collected from a power unit utilizing a limestone scrubber control system and burning a lignitic, high sulfur and ash content fuel which appears to contain a zinc mineral vein as evidenced by the zinc, lead, arsenic, and cadmium fuel composition (Table VII). These elemental contents are enriched by factors of 20 to 25 times in the fly ash collected at a stack port beyond the scrubber control system (see Tables II and III). This coal-fired fly ash is similar to oil-fired fly ash in respect to water solubility, total sulfate, and sulfuric acid, and, as determined by XRD and FT-IR analyses, metal sulfates and metal oxides. The differences between the scrubber-controlled power plant emissions and those from units using ESP controls are summarized in Table VIII.

An attempt was made to ascertain the possible effects of the scrubber-controlled system on the fly ash emission particulate composition by obtaining samples at the inlet to the scrubber and, as done previously, at the stack port after the scrubber. Unfortunately, operational problems were being experienced with the control system operation so that steady-state sampling was not possible and the samples obtained were more in the nature of grab samples. However, the results, shown in Table IX, indicate that the scrubber-control system is contributing to the formation of various sulfate species. A grab sample from the bottom of the scrubber consisted entirely of small 2 to 6 mm diameter black glassy iron and aluminum silicate spheroids, and no sulfate.

Conclusion

FT-IR spectroscopy has been found to be a useful adjunct to the more traditionally used XRD and chemical-phase techniques for the identification of inorganic compounds present in fly ash emissions. A present roadblock to facile

Table V. Possible Compound Compositions of Oil-Fired Fly Ash Samples Based on Chemical Analyses of Soluble and Insoluble Phases

calcd species	no. 1	no. 2	no. 4	no. 5	no. 6
C as C	12.4	63.7	21.5	1.5	14.5
H_2O [a]	7.0	5.0	4.5	5.5	2.0
H_2SO_4 [a]	0.1	0.2	0.05	1.0	1.5
NH_4 as $(NH_4)HSO_4$	0.08	0.83	5.18	1.03	46.6
Mg as MgO	22.8	3.8	1.6	0	0
Mg as $MgSO_4 \cdot H_2O$	26.8	6.6	28.5	14.8	13.6
V as V_2O_5	3.2	7.9	2.2	0	0.6
V as $VOSO_4 \cdot 3H_2O$	2.1	9.5	38.2	54.9	3.3
Fe as Fe_2O_3	0.45	0.2	0.3	0	0
Fe as $FeSO_4$	0.8	0.7	0.5	1.3	1.1
Ni as NiO	0.85	0.3	0.3	0	0.06
Ni as $NiSO_4$	2.65	1.6	2.8	6.0	0.8
Al as Al_2O_3	1.4	0.06	0.3	0.02	2.2
Al as $Al_2(SO_4)_3$	3.2	0.15	1.45	0	1.7
Si as SiO_2	0.55	0.4	0.45	0.05	0.5
Na as Na_2SO_4	12.1	0.95	1.55	6.25	0.6
K as K_2SO_4	0.3	0.2	0.2	0.2	0.25
Ca as CaO	0.55	0.2	0.04	0.01	0.2
Ca as $CaSO_4$	2.0	0.5	0.25	0.65	0.55
other elements as oxides/sulfates	1.3	0.35	0.75	1.0	1.0
totals of above	100.7	103.2	110.6	95.2	91.1
sulfates [b]	32.6	11.6	45.0	46.8	54.3

[a] H_2O and H_2SO_4 values are those determined as given in Table II rather than calculated values based on H. [b] SO_4^{2-} contents of the calculated species.

Table VI. Chemical Species Identified and Method Used for Oil-Fired Fly Ash Samples

species	method
carbon	determination by a combustion–GC method The absence of organics and carbonate forms together with microscopy and XRD analyses show the form to be uncombined, partially graphitic
H_2O	loss of weight at 105 °C
H_2SO_4	titration for strong acid
NH_4HSO_4	FT-IR and XRD
MgO	XRD
$MgSO_4 \cdot H_2O$	FT-IR and XRD
V_2O_5	XRD
$VOSO_4 \cdot 3H_2O$	FT-IR and XRD
Fe_2O_3	XRD
$FeSO_4 \cdot 7H_2O$	FT-IR and XRD
NiO	XRD
$NiSO_4$	FT-IR
Al_2O_3	XRD
$Al_2(SO_4)_3$	FT-IR
SiO_2	FT-IR and XRD
Na_2SO_4	FT-IR
K_2SO_4	FT-IR
CaO	XRD
$CaSO_4$	FT-IR

Table VII. Components of No. 4 Power Unit Fuel, Percent

S	ash	Zn	Pb	Cd	As
5.2	27.7	0.30	0.03	0.01	0.01

application of FT-IR can be overcome by the availability of a large literature library of reference compounds of known physical and chemical states. The FT-IR technique is applicable to the identification of amorphous as well as crystalline inorganic species, providing that suitable reference spectra are on hand.

The analytical data derived from the methodology application show that water-soluble sulfates are the predominant species present in oil-fired particulate emissions, and even coal-fired fly ash emissions contain significant quantities of water-soluble sulfates.

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Table VIII. Scrubber vs. ESP-Controlled Fly Ash Emissions

	scrubber, %	ESP, [a] %
water solubility	79.2	9–34
SO_4^{2-}	50.6	5–22
free H_2SO_4 acid	16.5	0.1–2
pH	2.2	2.7–11.3
selected trace metals		
Zn	7	0.03–0.12
Pb	0.74	0.007–0.015
Cd	0.22	0.001–0.0015
As	0.20	0.003–0.01
Sb	0.05	0.001–0.0015
Sn	0.05	0.001–0.002
compounds		
Fe–Al–silicate and Ca–Al–silicate glasses	10	70–90
α-quartz	5	1–10
Fe_2O_3	10	1–10
MgO		1–3
$CaSO_4$ anhydrous	10	1–10
$PbSO_4$	1	
$ZnSO_4 \cdot H_2O$	20	
H_2SO_4-acid	17	1–2

[a] Averages of no.'s 2, 3, and 5 coal-fired fly ashes.

Table IX. Scrubber Inlet and Outlet Fly Ash Sample Composition, Percent

	SO_4^{2-}	pH	water solubility	Zn	Pb	Cd	As
sample before scrubber	24.9	2.55	46.6	3.1	0.23	0.05	0.06
sample after scrubber	42.8	2.0	79.2	3.2	0.39	0.14	0.18

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Received for review July 5, 1979. Accepted January 21, 1980.